

dicubane (**5**) and dicubene (**8**) appear very similar structurally from the simple cube-based sketches in the text of this paper, in fact Figures 1 and 2 show them to be rather different. Since two, rather than four, carbon-carbon bonds fuse the two halves of the molecule in dicubene, dicubene occupies a much larger volume of space than does dicubane. This result is reinforced by the results of an evaluation of the total energy of dicubene at the dicubane equilibrium geometry. This exercise shows dicubene to lie 295 kcal/mol higher, i.e., dicubane is *not* a doubly excited electronic state of dicubene at the equilibrium geometry of the former.

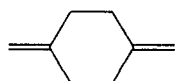
DZ+d SCF vibrational frequencies and IR intensities are given for dicubene in Table II, which proves that dicubene is a genuine minimum on the  $C_{12}H_8$  potential energy hypersurface at this level of theory. As with the much higher energy dicubane molecule, dicubene has several C-H vibrational stretching frequencies with significant IR intensities, namely  $\omega_{35}(B_{1u})$ ,  $\omega_{41}(B_{2u})$ , and  $\omega_{48}(B_{3u})$ .

The question of the existence of a barrier between **5** and the lower energy **8** cannot be unambiguously settled at the single configuration self-consistent-field level of theory. Some sort of post-Hartree-Fock theoretical treatment will be required for this purpose. However, the theoretical delicacy of such a barrier is illustrated by the research of Feller and Davidson<sup>13</sup> on the [2.2.2]propellane



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rearrangement to dimethylenecyclohexane



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Although Feller and Davidson report that the two-configuration SCF method predicts the stability of **9** to ring opening, their higher level configuration interaction (CI) method finds no minimum for [2.2.2]propellane. Experimentally, Eaton and Temme<sup>14</sup> have in fact isolated the dimethylcarboxamide derivative of [2.2.2]-propellane. We conclude that theoretical efforts to predict the absolute stability of dicubane (**5**) would not be profitable at this

(13) Feller, D.; Davidson, E. R. *J. Am. Chem. Soc.* 1987, 109, 4133.

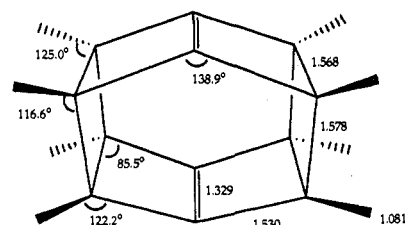
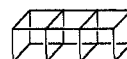


Figure 2. Predicted equilibrium geometries for the dicubene molecule (**7**,  $C_{12}H_8$ ). All bond distances are in Å.

time. This issue notwithstanding, the lower energy dicubene (**8**) remains an attractive synthetic target.

Should dicubane or some more favorable derivative (presumably one for which bulky R groups defend the four "unprotected" carbon atoms) be synthesized, one's imagination can readily construct a family of related molecules,<sup>15</sup> the first member of which might be called "tricubane".



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Of course, as the fused-cube structures in this family become longer, the eight R groups on the ends will become increasingly ineffective in protecting the highly strained interior carbon atoms.

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(14) Eaton, P. E.; Temme, G. H. *J. Am. Chem. Soc.* 1973, 95, 7508.

(15) This family of 3-dimensional molecules brings to mind the proposal of Liebman and Van Vechten of related 2-dimensional series of molecules, their "quadragonal ladders". See: Liebman, J. F.; Van Vechten, D. *Molecular Structure and Energetics*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: New York, 1987; Vol. 2, p 329.

(16) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H. *Chem. Phys. Lett.* 1989, 162, 165.

## Dinitrogen Sulfide ( $N_2S$ ) and Its Protonated Isomers

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**Abstract:** The protonation of  $N_2S$  offers a way of examining the nature of this simple, recently synthesized molecule. The conventional linear NNS, the less conventional NSN, and cyclic structures have been investigated with ab initio molecular quantum mechanical methods. Double- $\zeta$  plus polarization (DZP) and triple- $\zeta$  plus double polarization (TZ2P) basis sets have been used in conjunction with self-consistent-field (SCF), single and double excitation configuration interaction (CISD), and coupled cluster (CCSD) methods. The parent  $N_2S$  potential energy hypersurface is rather complicated, but for the protonated system no isomer lies within 30 kcal/mol of the  $NNSH^+$  global minimum.

### Introduction

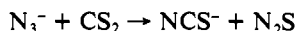
Although Powell<sup>1</sup> postulated the existence of  $N_2S$  in 1975 it was not until 1986 that Wentrup, Fischer, Maquestiau, and Flammang confirmed (via mass spectroscopy) the presence of  $N_2S$

as a decomposition product.<sup>2</sup> They also recorded an infrared band at  $2030\text{ cm}^{-1}$  which they assigned to the N-N stretch. Earlier Kass and DePuy had postulated that the reaction

(1) Powell, F. X. *Chem. Phys. Lett.* 1975, 33, 393.

(2) Wentrup, C.; Fischer, S.; Maquestiau, A.; Flammang, R. *J. Org. Chem.* 1986, 51, 1908.

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should occur with an estimated heat of formation for  $\text{N}_2\text{S}$  of 87.3 kcal mol<sup>-1</sup> or less.<sup>3</sup> Sensarma and Turner predicted a heat of formation of 47.6 kcal mol<sup>-1</sup> based on semiempirical MNDO calculations.<sup>4</sup> In 1988 Bender, Carnovale, Peel, and Wentrup reported the photoelectron spectrum of  $\text{N}_2\text{S}$  along with ab initio Hartree-Fock self-consistent-field (SCF) theoretical results.<sup>5</sup> They characterized  $\text{N}_2\text{S}$  as an S atom weakly bound to an  $\text{N}_2$  molecule. The lowest energy ionization was assigned to an N-N bonding, N-S antibonding  $\pi$  orbital. In a very recent paper, Brown, Elmes, and McNaughton<sup>6</sup> report the high-resolution IR spectrum of  $\text{N}_2\text{S}$ . They found the  $\nu_3$  vibrational frequency to be 2047.59 cm<sup>-1</sup>, and from rotational analysis they assigned  $\omega_2$  (the  $\pi$  bending mode) to 343 cm<sup>-1</sup> and inferred an N-N distance of 1.139 Å and an N-S distance of 1.578 Å.

Early theoretical work on  $\text{N}_2\text{S}$  includes the study of Collins and Duke, who found NNS to be the lowest energy isomer and obtained theoretical (SCF) bond lengths of 1.13 and 1.63 Å for N-N and N-S, respectively.<sup>7</sup> Laidlaw and Trsic used in Hartree-Fock-Slater method to study the singlet surface of NSN.<sup>8</sup> They note that reactions involving the transfer of an NSN fragment to or from sulfur-nitrogen systems raise the possibility of detection of a free NSN moiety.<sup>9</sup> Laidlaw and Trsic also found NNS to be the lowest energy isomer, and linear NSN the next higher structure, lying at about 48 kcal mol<sup>-1</sup>.

Although  $\text{N}_2\text{S}$  is analogous to  $\text{N}_2\text{O}$ , the replacement of the first-row oxygen by the second-row sulfur alters the bonding substantially. Two other analogues of  $\text{N}_2\text{O}$  that contain second-row atoms have also been recently prepared experimentally: PNO<sup>10</sup> and P<sub>2</sub>O.<sup>11</sup> The chemistry of these  $\text{N}_2\text{O}$  analogues is of interest in general, because second-row atoms, which form weak multiple bonds, nevertheless appear in situations that seem to require multiple bonding.  $\text{N}_2\text{S}$  is of particular interest because of the practical importance of nitrogen-sulfur compounds and reactions that might involve an  $\text{N}_2\text{S}$  fragment. We have undertaken a series of studies on the second-row analogues of  $\text{N}_2\text{O}$  and their protonated forms.<sup>12,13</sup> We report here the results of high-level ab initio theoretical studies of linear  $1^1\Sigma^+$  NNS,  $1^1A_1$  cyclic  $\text{N}_2\text{S}$ , and the various  $\text{HN}_2\text{S}^+$  isomers produced by protonation. We also report theoretical studies of the cyclic  $3^1B_2$  state and a multiconfigurational theoretical study of the singlet surface for bending linear NSN to form the cyclic  $\text{N}_2\text{S}$ .

## Methods

The standard Huzinaga-Dunning<sup>14,15</sup> double- $\zeta$  (DZ) basis and a more flexible contraction of the same primitive Gaussian functions (here labeled "triple- $\zeta$ " or TZ) represent starting points for this research. Polarization functions (i.e., d functions) with exponents of 0.80 for N and 0.50 for S were added to the DZ basis sets to give DZ + polarization (DZP) basis sets. Two sets of polarization functions with exponents of 1.60, 0.40 for N and 1.00, 0.25 for S were added to the TZ basis sets to give TZ2P basis sets. For the protonated systems, the additional polarization functions (hydrogen p functions) were  $\alpha_p(\text{H}) = 0.75$  (DZP) and  $\alpha_p(\text{H}) = 1.50, 0.375$  (TZ2P). Thus the TZ2P basis set may be designated H(4s2p/3s2p), N(9s5p2d/5s3p2d), S(11s7p2d/7s5p2d). All

- (3) Kass, S. R.; DePuy, C. H. *J. Org. Chem.* **1985**, *50*, 2874.  
 (4) Sensarma, S.; Turner, A. G. *Inorg. Chim. Acta* **1982**, *64*, L161.  
 (5) Bender, H.; Carnovale, F.; Peel, J. B.; Wentrup, C. *J. Am. Chem. Soc.* **1988**, *110*, 3458.  
 (6) Brown, R. D.; Elmes, P. S.; McNaughton, D. *J. Mol. Spectrosc.* **1990**, *140*, 390.  
 (7) Collins, M. P. S.; Duke, B. J. *J. Chem. Soc. Dalton Trans.* **1978**, 277.  
 (8) Laidlaw, W. G.; Trsic, M. *Inorg. Chem.* **1981**, *20*, 1792.  
 (9) Cheivers, T.; Oakley, R. T.; Wallace, A.; Swebston, P. *J. Chem. Soc., Chem. Commun.* **1980**, 35.  
 (10) Ahlrichs, R.; Schunk, S.; Schnöckel, H. *Angew. Chem.* **1988**, *27*, 421.  
 (11) (a) Andrews, L.; Withnall, R. *J. Am. Chem. Soc.* **1988**, *110*, 5605.  
 (b) Mielke, Z.; McCluskey, M.; Andrews, L. *Chem. Phys. Lett.* **1990**, *165*, 146.  
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 (13) Davy, R. D.; Schaefer, H. F. *J. Am. Chem. Soc.* Submitted for publication.  
 (14) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.  
 (15) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823.

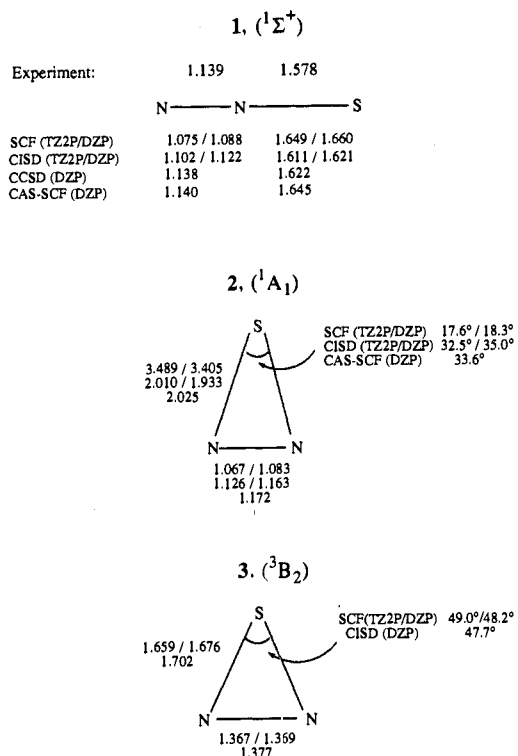


Figure 1. Theoretical geometries for the linear  $1^1\Sigma^+$ , cyclic  $1^1A_1$ , and cyclic  $3^1B_2$  isomers of  $\text{N}_2\text{S}$ . All bond distances are in Å.

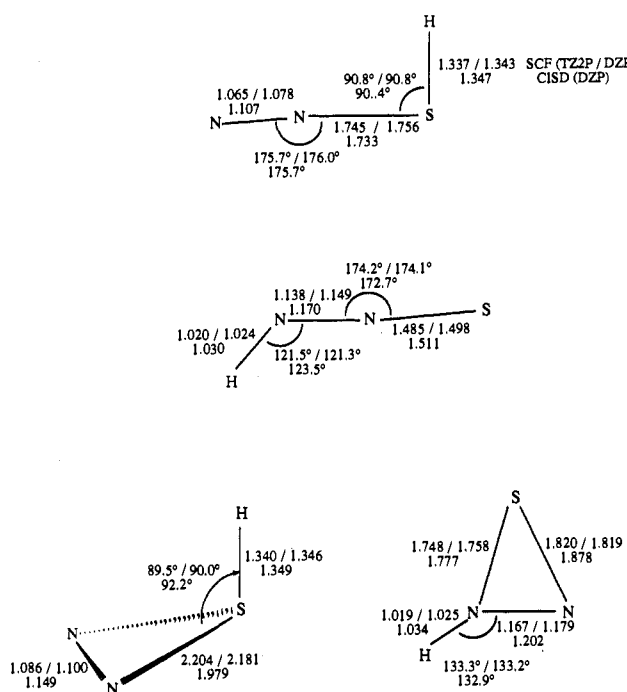


Figure 2. Theoretical geometries for the various isomers of protonated  $\text{N}_2\text{S}$ . All bond distances are in Å.

geometries were obtained via analytic first derivative methods. Self-consistent-field (SCF) vibrational frequencies were evaluated via analytic second derivatives. Vibrational frequencies for the methods of configuration interaction including all single and double excitations (CISD), coupled cluster including all singles and doubles (CCSD), and complete active space self-consistent-field (CAS-SCF) were determined by finite difference of analytic first derivatives. The SCF, CISD, and CCSD programs were those developed in our own group and coded in the PSI suite of programs.<sup>16</sup> The CAS-SCF method was that of Werner, Knowles, and Handy.<sup>17</sup> The CAS-SCF active space for the  $\text{N}_2\text{S}$  mol-

(16) PSI, distributed by PSITECH, Inc., Watkinsville, Georgia.

**Table I.** Theoretical Vibrational Frequencies (cm<sup>-1</sup>) and Total Energies (hartree) for the <sup>1</sup>Σ<sup>+</sup> State of Linear NNS and the <sup>1</sup>A<sub>1</sub> and <sup>3</sup>B<sub>2</sub> States of Cyclic N<sub>2</sub>S

	SCF		CISD		CCSD	CAS-SCF	experiment <sup>6</sup>
	DZP	TZ2P	DZP	TZ2P	DZP	DZP	
			$1\Sigma^+$ $N \equiv N - \bar{S}$				
$\omega_1$ NN stretch	2571	2568	2294	2318	2167	2081	$\nu = 2048$
$\omega_2$ NS stretch	588	594	713	709	712	661	
$\omega_3$ bend	487	484	480	493	461	447	$\sim 343$
energy	-506.38745	-506.40726	-506.84170 -506.89904 <sup>a</sup>	-506.94564 -507.01292 <sup>a</sup>	-506.94778	-506.57437	
			$^1A_1$ $\begin{array}{c} S \\   \\ N=N \end{array}$				
$\omega_1$ NN stretch	2703	2717	2001	2124		1849	
$\omega_2$ NS + NS stretch	29	22	366	173		243	
$\omega_3$ NS - NS stretch	75i	57i	518	452		409	
energy	-506.34752	-506.36793	-506.78188 -506.84040 <sup>a</sup>	-506.88282 -506.95014 <sup>a</sup>		-506.50961	
			$^3B_2$ $\begin{array}{c} S \\ \cdot \\ N-N \end{array}$				
$\omega_1$ 2NN - NS - NS	1213	1175	2018				
$\omega_2$ NN + NS + NS	849	852	533				
$\omega_3$ NS - NS	626	609	348				
energy	-506.26658	-506.28026	-506.71664 -506.77275 <sup>a</sup>				

<sup>a</sup> Indicates Davidson's corrections for unlinked quadruple excitations.<sup>22</sup>

ecule included all molecular orbitals constructed from the 2s and 2p atomic orbitals of nitrogen, and the 3s and 3p atomic orbitals of sulfur. Thus, the active space included 16 electrons in 12 molecular orbitals.

### Results and Discussion

The theoretical geometries of the isomers of N<sub>2</sub>S are given in Figure 1. The total energies and theoretical vibrational frequencies are given in Table I. The theoretical geometries of the isomers of protonated N<sub>2</sub>S are given in Figure 2, and their total energies and frequencies are given in Table II. The relative energies of the nonprotonated and protonated isomers are given in Tables III and IV, respectively.

**A. Linear NNS.** Our SCF results (and all previous SCF investigations) greatly underestimate the degree of N-S bonding and overestimate the extent of N-N bonding. The SCF N-N bond is 0.05 Å shorter, and the SCF N-S bond is 0.08 Å longer, than the experimental values. The scaling factor usually applied to SCF vibrational frequencies ( $\sim 0.9$ )<sup>18</sup> leaves the N-N stretch still about 13% too high. The bending frequency is also much larger than the approximate experimental value. It seems clear that an accurate theoretical picture of NNS requires correlated methods.

Theoretical methods that include electron correlation usually give bonds longer than those predicted at the SCF level. The N-N bond behaves typically—the match to experiment is quite good for the CISD method, and excellent for the DZP CCSD level of theory, i.e., 1.138 vs 1.139 Å experimentally. Furthermore, the DZP CCSD N-N harmonic stretching vibrational frequency (2167 cm<sup>-1</sup>) is in quite reasonable agreement with the experimental fundamental (2048 cm<sup>-1</sup>).<sup>6</sup> Given the earlier reported<sup>6</sup> poor agreement between SCF theory and experiment for the N-N stretching, the vast improvement offered by CCSD theory is very encouraging.

The theoretical N-S bond length, however, is shorter than the SCF distance at correlated levels; and the CISD and CCSD stretching frequencies are larger than the comparable SCF predictions. Typically, theoretical determinations of bond lengths are "helped out" by a cancellation of errors. Basis set deficiencies typically result in the overestimation, and lack of complete electron correlation results in the underestimation of the length of a bond.<sup>19</sup>

The N-S bond in NNS is unusual because correlation actually shortens the bond. This is due, in large part, to the nature of the lowest unoccupied molecular orbital (LUMO). The LUMO is a  $\pi$  N-N antibonding but nearly N-S nonbonding orbital. Because basis set and correlation are not opposing one another, there is a lesser degree of cancellation of errors for the N-S bond. The N-S bond length at the TZ2P CISD and DZP CCSD levels is too long by about 0.024 and 0.035 Å, respectively.

Brown and co-workers<sup>6</sup> estimated the harmonic bending vibrational frequency to be 343 cm<sup>-1</sup>, but we predict a higher frequency even at the most reliable levels of theory—493 cm<sup>-1</sup> at TZ2P CISD, and 461 cm<sup>-1</sup> at DZP CCSD. We suspect that the experimental frequency is somewhat too low for two reasons. First, larger basis sets actually increase this frequency, and increasingly sophisticated treatments (CISD  $\rightarrow$  CCSD) of electron correlation decrease the bending frequency very little; thus incompleteness in the theoretical method may not favor a radically lower frequency. Second, the DZP CAS-SCF frequency (447 cm<sup>-1</sup>) is expected<sup>20</sup> to be fortuitously close to experiment, because CAS-SCF typically underestimates bond strengths, and the N-S bond distance is here substantially too long (1.645 Å), which should cause further underestimation of the bending frequency.

**B. Cyclic N<sub>2</sub>S.** The cyclic isomer of N<sub>2</sub>O has been predicted theoretically to lie over 75 kcal mol<sup>-1</sup> above NNO.<sup>21</sup> Theoretical studies of P<sub>2</sub>O and PNO show that these second-row analogues have much lower relative energies for the cyclic isomers. The same conclusion is found here to hold true for N<sub>2</sub>S. The SCF method, however, does not give a cyclic minimum, but rather a very weakly bound transition state for the migration of sulfur from one nitrogen to the other. The earlier Hartree-Fock-Slater study of Laidlaw and Trsic also found no minimum for cyclic N<sub>2</sub>S.<sup>8</sup> However, when electron correlation is included the cyclic structure is a minimum, with all three of its vibrational frequencies being real. Electron correlation dramatically shortens the N-S bonds and clearly indicates a theoretically stable molecule. The linear-cyclic energy

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(20) See, for example: Xie, Y.; Davy, R. D.; Yates, B. F.; Blahous, C. P.; Yamaguchi, Y.; Schaefer, H. F. *Chem. Phys.* **1989**, *135*, 179.

(21) Lathan, W. A.; Radom, L.; Hariharan, P. C.; Hehre, W. J.; Pople, J. A. *Top. Cur. Chem.* **1973**, *40*, 1.

(17) Knowles, P. J.; Werner, H. J. *Chem. Phys. Lett.* **1985**, *115*, 259.

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**Table II.** Theoretical Vibrational Frequencies (cm<sup>-1</sup>) and Energies (hartree) for Protonated N<sub>2</sub>S Isomers

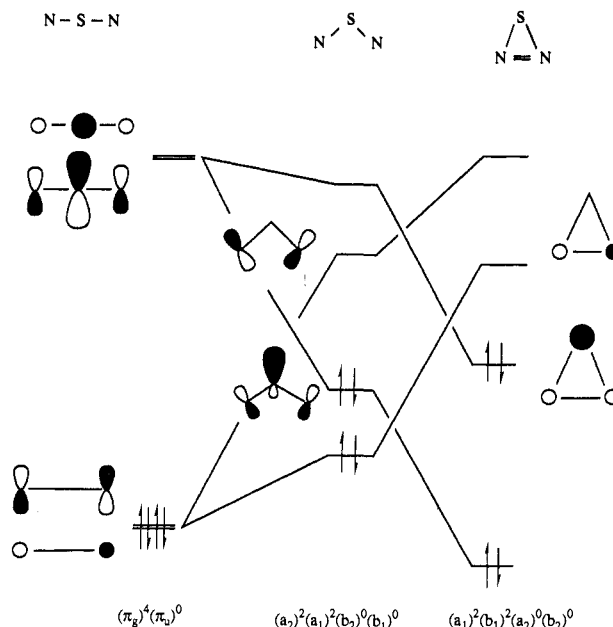
	SCF		CISD
	DZP	TZ2P	DZP
$\left[ \text{N} \equiv \text{N} - \overset{\text{H}}{\text{S}} \right]^+$			
$\omega_1$ SH stretch	2799	2813	2750
$\omega_2$ NN stretch	2725	2721	2467
$\omega_3$ NSH bend	1105	1118	1071
$\omega_4$ SN stretch	515	516	552
$\omega_5$ out-of-plane bend	397	391	388
$\omega_6$ NNS bend	355	340	346
energy	-506.66738	-506.69206	-507.12095 -507.17742 <sup>a</sup>
$\left[ \overset{\text{H}}{\text{N}} = \text{N} = \text{S} \right]^+$			
$\omega_1$ NH stretch	3556	3515	3519
$\omega_2$ NN stretch	2147	2139	2081
$\omega_3$ NS stretch	1004	1014	959
$\omega_4$ HNN bend	919	926	829
$\omega_5$ out-of-plane bend	509	524	492
$\omega_6$ NNS bend	482	504	465
energy	-506.60395	-506.62637	-507.07866 -507.14233 <sup>a</sup>
$\left[ \overset{\text{H}}{\text{S}} \right]^+$			
$\omega_1$ SH stretch	2790	2804	2751
$\omega_2$ NN stretch	2516	2523	2105
$\omega_3$ H out-of-plane bend	905	883	1010
$\omega_4$ NSH - NSH asym bend	279	266	749
$\omega_5$ NS - NS asym stretch	223	234	465
$\omega_6$ NS + NS sym stretch	142	120	316
energy	-506.61353	-506.64051	-507.06537 -507.12369
$\left[ \overset{\text{S}}{\text{H}} \right]^+$			
$\omega_1$ NH stretch	3547	3529	
$\omega_2$ NN stretch	1987	1968	
$\omega_3$ HNN bend	1244	1265	
$\omega_4$ H out-of-plane bend	752	779	
$\omega_5$ (H)NS stretch	741	737	
$\omega_6$ NS stretch	578	566	
energy	-506.55466	-506.57405	-507.01906 -507.07999 <sup>a</sup>

<sup>a</sup> Includes Davidson's correction for unlinked quadruple excitations.**Table III.** Energies (kcal mol<sup>-1</sup>) of the <sup>1</sup>A<sub>1</sub> and <sup>3</sup>B<sub>2</sub> States of Cyclic N<sub>2</sub>S Relative to the Linear <sup>1</sup>Σ<sup>+</sup> State of NNS

	$\text{N} \equiv \text{N} - \overset{\text{S}}{\text{H}}$	$\text{N} \equiv \text{N} \begin{matrix} \text{S} \\ \diagup \end{matrix}$	$\begin{matrix} \text{S} \\ \diagup \end{matrix} \text{N} = \text{N} \cdot$
SCF			
DZP	0.0	25.0 <sup>a</sup>	75.8
TZ2P	0.0	24.7 <sup>a</sup>	79.7
CISD			
DZP	0.0	37.5 (36.8) <sup>b</sup>	78.5 (79.2) <sup>b</sup>
TZ2P	0.0	39.4 (39.4) <sup>b</sup>	
CAS-SCF			
DZP	0.0	40.9	

<sup>a</sup> Cyclic structure is a transition state at the SCF level. <sup>b</sup> Includes Davidson's correction for unlinked quadruple excitations.<sup>22</sup>

difference is larger at correlated levels of theory, about 40 kcal mol<sup>-1</sup> compared to about 25 kcal mol<sup>-1</sup> for the SCF method, but still much less than that predicted<sup>21</sup> for N<sub>2</sub>O. The bonding in cyclic N<sub>2</sub>S consists essentially of donation from the N-N π bond to an

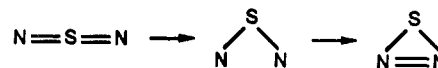
**Figure 3.** Qualitative molecular orbital diagram for bending linear NSN to cyclic N<sub>2</sub>S.**Table IV.** Theoretical Relative Energies (kcal mol<sup>-1</sup>) of the Various Protonated N<sub>2</sub>S Isomers

isomer	SCF		CISD
	DZP	TZ2P	DZP
[NNSH] <sup>+</sup>	0.0	0.0	0.0 (0.0) <sup>a</sup>
[HNNS] <sup>+</sup>	39.8	41.2	26.5 (22.0) <sup>a</sup>
$\left[ \overset{\text{H}}{\text{S}} \right]^+$	33.8	32.3	34.8 (33.7) <sup>a</sup>
$\left[ \overset{\text{S}}{\text{H}} \right]^+$	70.7	74.0	63.9 (61.1) <sup>a</sup>

<sup>a</sup> Includes Davidson's correction for unlinked quadruple excitations.<sup>22</sup>

empty sulfur 3p orbital and the back donation from a filled sulfur 3p orbital into an empty N-N π\* molecular orbital; the sulfur is oxidizing the N-N π bond. Given the strength of the N-N π bond and the weak electronegativity of sulfur, one would expect the N-S bonds to be weak in cyclic NS<sub>2</sub>.

As noted in the Introduction, the study of Laidlaw and Trsic was prompted by the possible transfer of an NSN fragment in certain reactions. A symmetric N<sub>2</sub>S molecule has never been detected experimentally, but the stability of cyclic N<sub>2</sub>S at correlated levels of theory led us to reconsider the potential energy curve for bending of symmetric N<sub>2</sub>S:



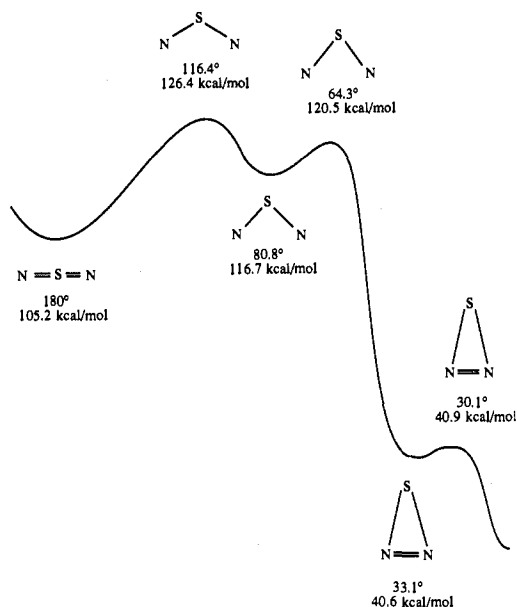
This transformation involves the promotion of two electrons from a b<sub>2</sub> to an a<sub>1</sub> molecular orbital in going from linear NSN to bent (90°) and another crossover from a<sub>2</sub> to b<sub>1</sub> for bent to cyclic. This is shown in Figure 3. Such orbital crossings necessitate a multiconfigurational approach; thus, the CAS-SCF method was used to construct a potential curve for bending, which is given in Figure 4. The importance of an MCSCF approach may also be deduced from Laidlaw and Trsic's Figure 1, which displays crossings of the single configuration total energies. The present theoretical geometries, energies, and vibrational frequencies of the stationary points on the curve are given in Table V.

The CAS-SCF potential curve differs in several ways from the Hartree-Fock-Slater (HFS) curve obtained by Laidlaw and Trsic. First, the linear symmetric NSN structure lies at 105 kcal mol<sup>-1</sup> (versus NNS) in the CAS-SCF approximation, but was only 48 kcal mol<sup>-1</sup> higher in the HFS method.<sup>8</sup> (Our more conventional

**Table V.** Theoretical Geometries, Vibrational Frequencies, and Energies for N<sub>2</sub>S Stationary Points Along the Bending Potential Energy Curve at the DZP CAS-SCF Level of Theory<sup>a</sup>

	linear	linear/bent TS	bent	bent/cyclic TS	cyclic	cyclic dissociation TS
N-S	1.510	1.618	1.620	1.690	2.025	2.208
NSN	180.0	116.4	80.8	64.3	33.1	30.1
sym stretch	954	754	890	829	1849 <sup>b</sup>	2045 <sup>b</sup>
bend	166	392i	309	714i	243 <sup>c</sup>	170i <sup>c</sup>
energy	-506.40677	-506.38237	-506.38838	-506.38237	-506.50961	-506.50908

<sup>a</sup> Bond distances are in Å and angles are in deg. For a qualitative sketch, see Figure 4. <sup>b</sup> Corresponds to NN stretch. <sup>c</sup> Corresponds to NS + NS symmetric stretch.



**Figure 4.** DZP CAS-SCF potential energy curve for bending on the singlet surface of NSN. The symmetric vibrational modes were evaluated, but stationary points are assumed to be stable with respect to asymmetric (symmetry breaking) modes.

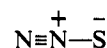
basis set formulated SCF method also gives a much higher relative energy than Laidlaw and Trsic for linear NSN, +125 kcal mol<sup>-1</sup> with a DZP basis.) This is somewhat surprising, especially since the bond lengths are similar in the two methods: 1.50 (CAS-SCF) vs 1.47 Å (HFS). Second, the HFS method does not find a minimum for the cyclic form. This is less surprising, since electron correlation is necessary to correctly predict the stability of this isomer.

The present DZP CASSCF potential curve (Figure 4) suggests that any NSN fragment generated with a bond angle less than about 115° will go to the bent rather than linear structure. The NSN angle was 108° in the experimental crystal structure fragment considered by Laidlaw and Trsic;<sup>8</sup> at this angle the excess vibrational energy should allow traversal of the bent-to-cyclic barrier. The CAS-SCF gives a very small barrier (about 0.3 kcal mol<sup>-1</sup>) for dissociation of the cyclic form to N<sub>2</sub> and singlet S atom. Although further correlation at the CI or CC levels should deepen the cyclic potential well, the excess energy may nevertheless be enough to cause dissociation. That is, the cyclic form of N<sub>2</sub>S may not be a stable entity. To produce a stable NSN fragment, the NSN angle should be greater than 115°, thus trapping the molecule in the potential well of the linear structure.

Earlier theoretical studies found several excited states of linear NNS to be dissociative.<sup>22</sup> However, promoting an electron from the HOMO to the LUMO does give a bound triplet excited state for the cyclic isomer. This is, in part, an N-N π to π\* transition. As shown in Figure 3, the HOMO is a b<sub>1</sub> symmetry π orbital and is N-N bonding, but N-S antibonding; the LUMO is the a<sub>2</sub> symmetry N-N π antibonding orbital. The triplet lies about 40

kcal mol<sup>-1</sup> higher than the cyclic singlet at the DZP CISD level and has a longer N-N bond and shorter N-S bonds. Because the weaker N-S bond is strengthened in the triplet state, the cyclic triplet might be kinetically more stable than the singlet, although it is thermodynamically less favored. Thus, photolytic production of an NSN species might be more likely to lead to detectable cyclic NSN.

**C. Protonated N<sub>2</sub>S.** On the basis of the strength of the N-N bond in N<sub>2</sub>S, the resonance structure



is dominant, despite the greater electronegativity of nitrogen. One would predict on this basis that protonation at sulfur would be favored. This is indeed the case at all levels of theory used here. Protonation at sulfur increases N-N π bonding at the expense of the N-S π bond; protonation at sulfur shortens the N-N distance by about 0.015 Å at the DZP CISD level. Protonation at nitrogen favors the opposite: oxidation of the N-N π bond and a stronger N-S π bond. Furthermore, protonation at nitrogen lengthens the N-N bond substantially, by about 0.05 Å at the DZP CISD level. In related work, Carroll, Chang, and Bader<sup>23</sup> compared the theoretical geometries (obtained at the 6-31G\*\* SCF level of theory) of base-hydrofluoric acid complexes with the geometry predicted by the Laplacian of the charge density of the base. NNS was a rare case for which the geometry predicted by the Laplacian did not qualitatively match the theoretically optimized geometry. For NNS the acidic hydrogen was attached to the sulfur atom, although the Laplacian predicted that the greatest available charge density was in a nitrogen σ type molecular orbital. For NNS, the present theoretical charge distribution also incorrectly favors protonation at the terminal N; the Mulliken charges for NNS are -0.10, +0.14, and -0.04 for N (terminal), N (center), and S, respectively, at the DZP CCSD level, but the bonding, especially the relative energy of the S-N and N-N π bonds, strongly favors protonation at sulfur. Clearly, electrostatic considerations are not infallible in predicting sites of protonation.

Protonation at sulfur is also favored for cyclic N<sub>2</sub>S. The energy difference between N and S protonation is nearly the same for cyclic and linear N<sub>2</sub>S. Protonation of cyclic N<sub>2</sub>S radically alters the theoretical N-S bond lengths at the SCF level, but this is due to the previously mentioned inadequacy of the SCF method for cyclic N<sub>2</sub>S. Comparisons at the DZP CISD level show that protonation at sulfur shortens the N-S bonds by 0.03 Å and lengthens the N-N bond by about 0.02 Å. This is consistent with the proton partially oxidizing the N-S antibonding, N-N bonding HOMO. Protonation at nitrogen shortens both N-S bonds much more than sulfur protonation. The (H)N-S bond is shortened by 0.23 Å and the N-S bond opposite the protonation site is shortened by 0.13 Å. For N<sub>2</sub>S it thus seems that any change that strengthens the N-S bonds at the expense of the very strong N-N bond raises the total energy.

### Concluding Remarks

Theoretical bond lengths and vibrational frequencies of linear and cyclic N<sub>2</sub>S have been obtained. Good agreement with the

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very recent experimental results<sup>6</sup> for linear N<sub>2</sub>S is found for most parameters; however, the estimated experimental bending harmonic vibrational frequency is 100 cm<sup>-1</sup> below the two most reliable theoretical estimates (obtained using the DZP CASSCF and DZP CCSD methods). Protonation of the linear isomer is favored at sulfur, and will weaken the N-S bond. Unlike P<sub>2</sub>O, protonation does not dramatically lower<sup>13</sup> the relative energy of cyclic N<sub>2</sub>S. Protonation of N<sub>2</sub>S lowers the relative energy of the cyclic form by only 3.1 kcal mol<sup>-1</sup> at the DZP CISD+Q level (Q refers to Davidson's correlation for quadrupole excitations<sup>24</sup>). For cyclic P<sub>2</sub>O, protonation disrupts the weak P-P bond, whereas the

strong N-N bond is disrupted in N<sub>2</sub>S. Although protonation gives little thermodynamic stabilization to cyclic N<sub>2</sub>S, it may, in a way similar to excitation to the triplet state, provide kinetic stabilization. The N-S bonds are the most easily broken, and protonation of cyclic N<sub>2</sub>S strengthens those bonds. One may, therefore, have a better chance of observing cyclic N<sub>2</sub>S by protonating the parent compound. Linear N<sub>2</sub>S, on the other hand, is more likely to fall apart upon protonation, because protonation will most likely occur at sulfur, leading to faster loss of N<sub>2</sub>.

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## Ion Association and Electric Field Effects on Electron Hopping in Redox Polymers. Application to the Os(bpy)<sub>3</sub><sup>3+/2+</sup> Couple in Nafion

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**Abstract:** The high ionic content and low dielectric constant that prevail in the interior of many redox polymers might be expected to accentuate the extent of ionic association within the polymers. The present study is an attempt to investigate the effects of ionic association on the dynamics of electron hopping within such materials. The general concepts of the treatment are exemplified by the experimental system chosen for study: the Os(bpy)<sub>3</sub><sup>3+/2+</sup> redox couple incorporated in Nafion films on electrode surfaces. Extensive ion association between both halves of the redox couple and the fixed anionic groups in the Nafion is argued to be responsible for the irreversibility of the incorporation. The apparent diffusion coefficient, which reflects the dynamics of electron propagation in the films, exhibits a remarkably sudden increase as the quantity of the redox couple in the film approaches electrostatic saturation with respect to the fixed anionic sites present. The observed behavior is not satisfactorily accounted for by previous models which have been proposed, even those that take account of the presence of electric fields within the films. The introduction of ionic association into the model for electron propagation leads to predictions that are in accord with the observed behavior. A key ingredient in the successful model is the assumption that the predominant forms of the electroactive counterions incorporated in Nafion are neutral aggregates resulting from association with several of the fixed anionic sites. Dissociation of the fully associated, neutral, oxidized half of the redox couple into a singly charged species which is associated with the same number of fixed anionic sites as the predominant form of the reduced half of the redox couple prior to electron self-exchange appears to be the lowest energy pathway for this process. The presence of ionic association equilibria which control such prior dissociation provides a satisfactory explanation for the steep increase in the apparent diffusion coefficient, i.e., in the rate of electron self-exchange between pairs of the incorporated redox couple, as the concentration approaches the saturation value. The steep increase results from a shift in the ion association equilibrium to produce more of the partially dissociated, oxidized half of the redox couple, which is the best partner for accepting an electron from the fully associated, reduced half of the redox couple. The inevitable electric fields present within the polyelectrolyte films also affect the observed behavior, especially as the concentration of incorporated electroactive counterions is increased, but the simultaneous presence of ionic association is required to produce predicted behavior which matches that observed experimentally.

The mechanisms that determine the rates of charge propagation within polymers containing covalently, coordinatively, or electrostatically bound redox centers have attracted active attention since the earliest applications of these materials as electrode coatings.<sup>2-15</sup> Besides their intrinsic interest, these mechanisms

are also important in view of the electrocatalytic properties<sup>16</sup> of such films, because charge propagation (together with the rate

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